Report for 2003NJ43B: Development of Supported Liquid Membrane Micro-Extraction (SLMME) followed by Ion-Pair Chromatography (IPC) for analysis of halo-acetic acids (HAAs) and chlorinated acid herbicides (CAHs) in water

- Conference Proceedings:
  - Somenath Mitra, Dawen Kou and Xiaoyan Wang Supported Liquid Membrane Micro-Extraction (SLMME) with HPLC Detection for the Monitoring Trace Haloacetic Acids in Water Presented at: 42nd Annual Eastern Analytical Symposium, Nov. 2003, Somerset, NJ
  - Somenath Mitra, Dawen Kou and Xiaoyan Wang Interfacing membrane Extraction with HPLC for Continuous On-line Monitoring Presented at: 42nd Annual Eastern Analytical Symposium, Nov. 2003, Somerset, NJ
- Other Publications:
  - Xiaoyan Wang, Dawen Kou, Edmund J. Bishop and Somenath Mitra Supported Liquid Membrane Micro-Extraction (SLMME) for the Determination of Trace Organic Acids. Posted at: 227th ACS National Meeting, March 2004, Anaheim, CA
- Articles in Refereed Scientific Journals:
  - Dawen Kou, Xiaoyan Wang and Somenath Mitra Supported Liquid Membrane Micro-Extraction (SLMME) with HPLC-UV Detection for Monitoring Trace Haloacetic Acids in Water Submitted to Journal of Chromatography A. (2004), in review

Report Follows

Annual Report submitted to USGS/NJWRRI (Year 2003)

Development of Supported Liquid Membrane Micro-Extraction (SLMME) followed by Ion-Pair Chromatography (IPC) for analysis of halo-acetic acids (HAAs) and chlorinated acid herbicides (CAHs) in water

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Research Objectives:

The objective of this study is to develop an analytical method for the continuous on-line monitoring haloacetic acids, which is the major group of the nonvolatile disinfection byproducts (DBPs) in drinking water [1]. Table 1 lists the names, formula, acronyms and properties of the nine HAAs [2]. Continuous supported liquid membrane extraction (SLME) followed by high performance liquid chromatography is designed for the on-line monitoring. This technique is automated, fast, and eco-friendly, i.e., it uses minimum amount of organic solvent and other chemicals. This technique provides high enrichment factors for real-time monitoring, and the liquid membrane is inexpensive and is easy to be regenerated.

Table 1. Names, Formula, Acronyms, and Properties of Haloacetic Acids

Names	Formula	Abbreviation	pKa	LogP
Monochloroacetic acid	$ClCH_2COOH$	MCAA	2.87	0.22
Dichloroacetic acid	$Cl_2CHCOOH$	DCAA	1.26	0.92
Monobromoacetic acid	$BrCH_2COOH$	MBAA	2.89	0.41
Bromochloroacetic acid	$BrClCHCOOH$	BCAA	1.39	1.14
Dibromoacetic acid	$Br_2CHCOOH$	DBAA	1.47	1.69
Trichloroacetic acid	Cl_3CCOOH	TCAA	0.51	1.33
Bromodichloroacetic acid	$BrCl_2CCOOH$	BDCAA	1.09	2.31
Chlorodibromoacetic acid	$ClBr_2CCOOH$	CDBAA	1.09	2.91
Tribromoacetic acid	Br_3CCOOH	TBAA	2.13	3.46

Methodology:

Figure 1 shows the system of continuous supported liquid membrane extraction followed by online HPLC-UV detection. It includes a hollow fiber membrane module, two pumps and a HPLC system. The first pump (a Hewlett-Packard 1050 HPLC pump) was used for the delivery of the acceptor (0.05 M tris buffer PH=8.7) and the other (a Beckman 110B pump) for the acidified HAAs water sample. A timer controlled six-port HPLC injection valve (Valco Instruments Co. Inc., Houston TX) was used to make automatic injections into a Hewlett-Packard 1050 HPLC system with a Waters 486 tunable absorbance UV detector. The wavelength was set at 210nm. Water sample flowed

through the shell side of the membrane module while the acceptor flowed inside the hollow fiber lumen. The HAAs molecules in the water sample were extracted and enriched into the acceptor. The extract was injected automatically into the HPLC system by a timer controlled six-port injection valve every fifteen minutes. The sample loop volume was 20 μl. Minichrom V 1.62 software (VG Data System) was used for data acquisition.

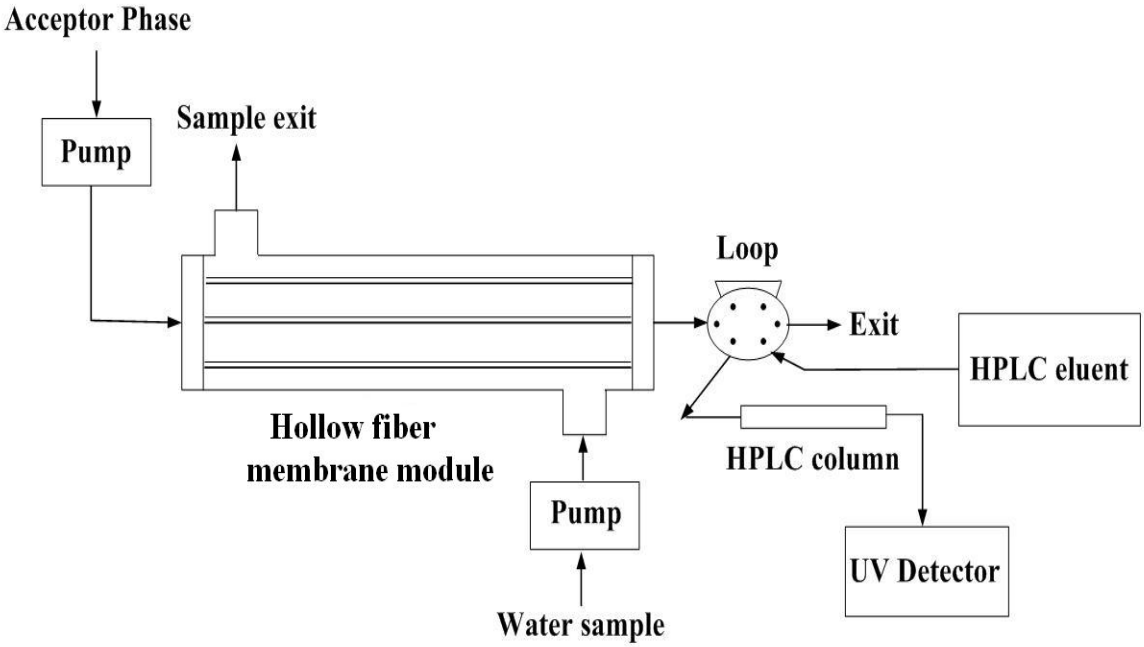

Figure 1. Schematic diagram of continuous supported liquid membrane extraction followed by HPLC-UV detection.

The membrane module for SLME was made with by packing three pieces of 130 cm long hollow fiber membrane into a Teflon tube. The membrane was Celgard® X20 (Hoechst Celanese, Charlotte, NC). It had an I.D. of 400 μm and an O.D. of 460 μm, with an average pore size of 0.03 μm and porosity of 40%. The membranes were soaked with membrane liquid (5% trioctylphosphine oxide in Di-hexyl ether) before fixed into the system. The HPLC column used here was a 150 mm × 4.6 mm YMC ODS-A C18 column with 3 micron packing. The HPLC mobile phase was 95:5 (v/v) 15 mM KH_2PO_4 (PH 2.2): Acetonitrile at a flow rate of 1.0 ml/min. Only 0.75 ml acetonitrile was consumed per HPLC run (5%*1ml/min*15min=0.75ml).

Principal Findings and Significance:

The effects of the acceptor flow rate on enrichment factor (EF) and extraction efficiency (EE%) in continuous SLME were studied. The flow rate of water sample was kept constant at 1 ml/min, while the acceptor flow rate was changed from 0.005 ml/min to 0.02 ml/min. The acceptor was first collected and the volume was measured. It was found that the loss of acceptor during extraction was negligible. Thus the experiment was

carried out online with HPLC-UV detection. EF and EE (%) as a function of the acceptor flow rate are shown in Figure 2 and Figure 3 respectively. EF decreased significantly with the increase of the donor flow rate. At a lower flow rate, the contact time of the analytes with the acceptor increased, thus relatively more analytes could be trapped into the acceptor. Also with a lower acceptor flow rate the concentrations of analytes were higher than in with a higher flow rate because of the less volume of acceptor. The EE increased with acceptor flow rate increase from 0.005 ml/min to 0.015 ml/min, then decreased as the acceptor flow rated increased to 0.02 ml/min.

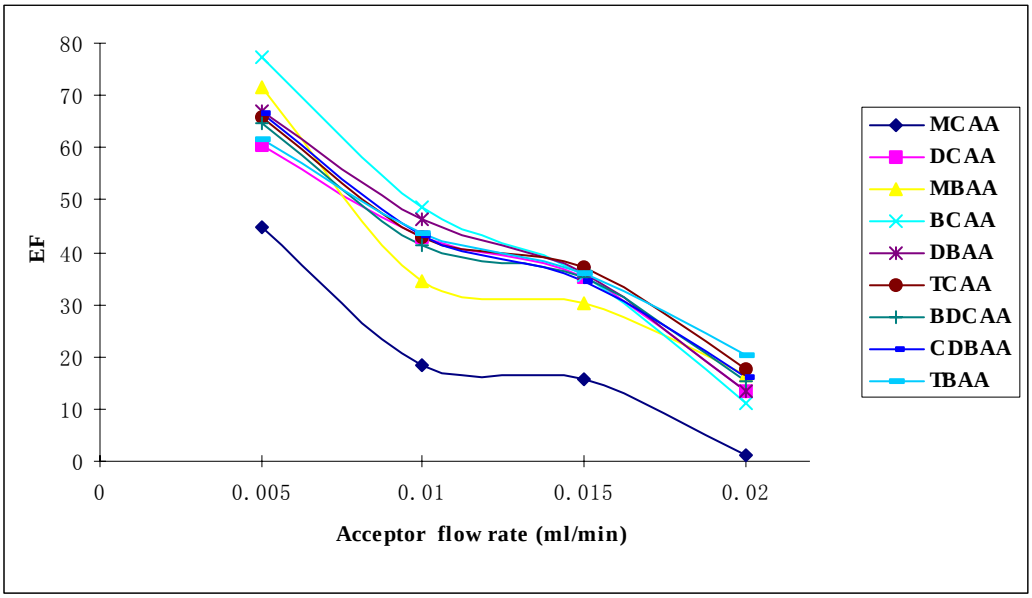

Figure 2. EF as a function of acceptor flow rate, the donor flow rate was kept constant at 1 ml/min.

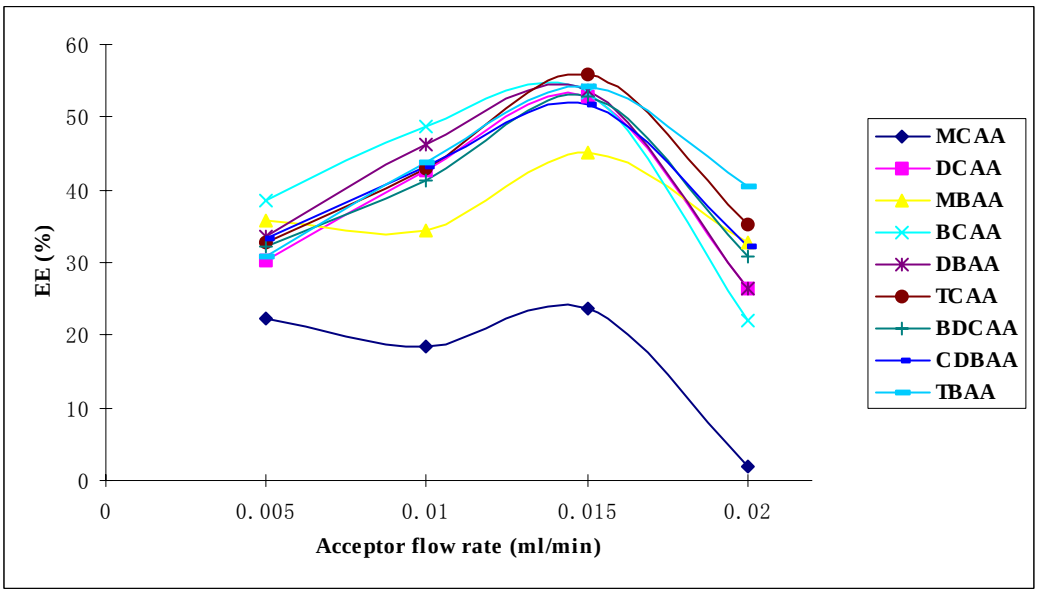

Figure 3. EE (%) as a function of acceptor flow rate, the donor flow rate was kept constant at 1 ml/min.

The effects of the donor flow rate on EF and EE was also studied. The acceptor flow rate was kept constant at 0.005 ml/min, while the donor flow rate was increased from 1 ml/min to 4 ml/min. Analysis was performed online. EF as a function of the donor flow rate is shown in Figure 4. EF increased dramatically as the flow rate of water sample increased from 1 ml/min to 4 ml/min. With a higher donor flow rate, more analytes contacted the membrane, thus resulting in more analytes trapped in the acceptor, which led to higher EF. EE increases with the increase of EF but decreases with the increase of the donor flow rate, the result is shown in Figure 5.

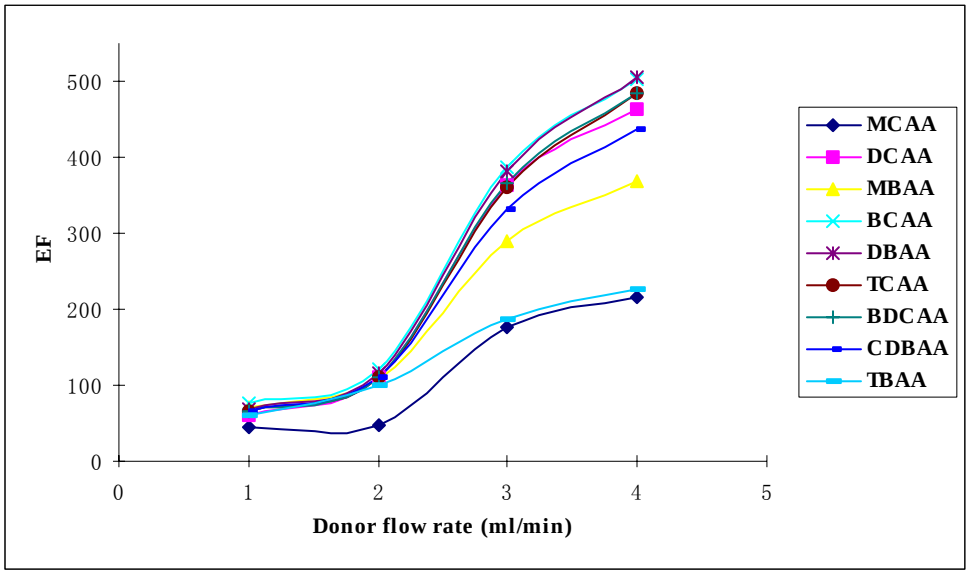

Figure 4. EF as a function of water sample (Donor) flow rate, the flow rate of acceptor was kept constant at 0.005 ml/min

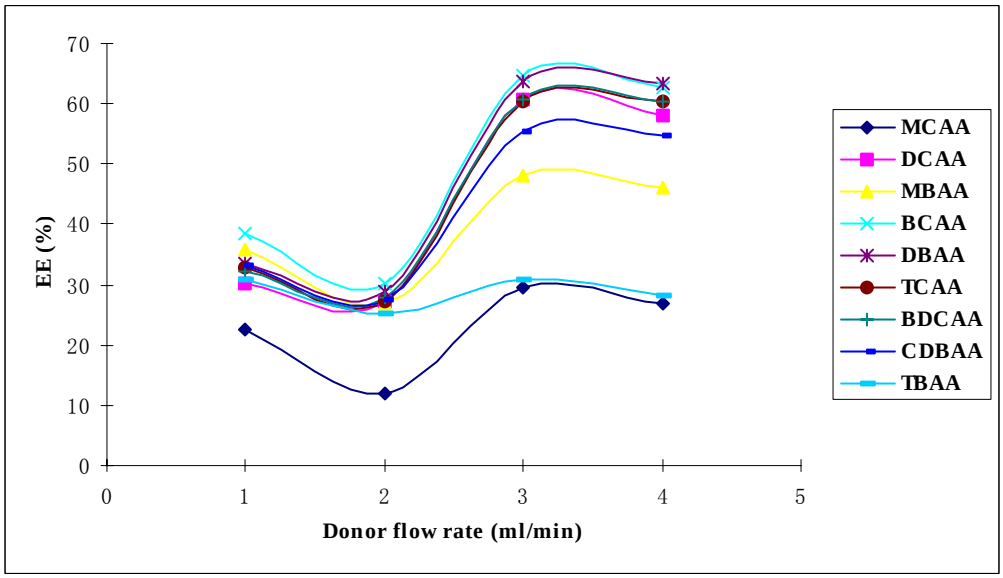

Figure 5. EE (%) as a function of water sample (Donor) flow rate, the flow rate of acceptor was kept constant at 0.005 ml/min

The continuous online monitoring of nine HAAs was performed by SLME combined with online HPLC-UV detection. The HAAs in acidified donor were extracted and trapped in alkaline acceptor. The enriched acceptor was automatically injected into the HPLC-UV system every fifteen minutes by the timer controlled six-port injection valve. Sequential chromatograms were obtained and shown in Figure 6. The donor was a water sample (PH=1.9) containing 80 ng/ml (ppb) of nine HAAs. The donor flow rate was 4 ml/min. The acceptor was 0.05 M tris buffer (PH 8.7) at a flow rate of 0.005 ml/min. Good reproducibility in peak shape and retention time were observed.

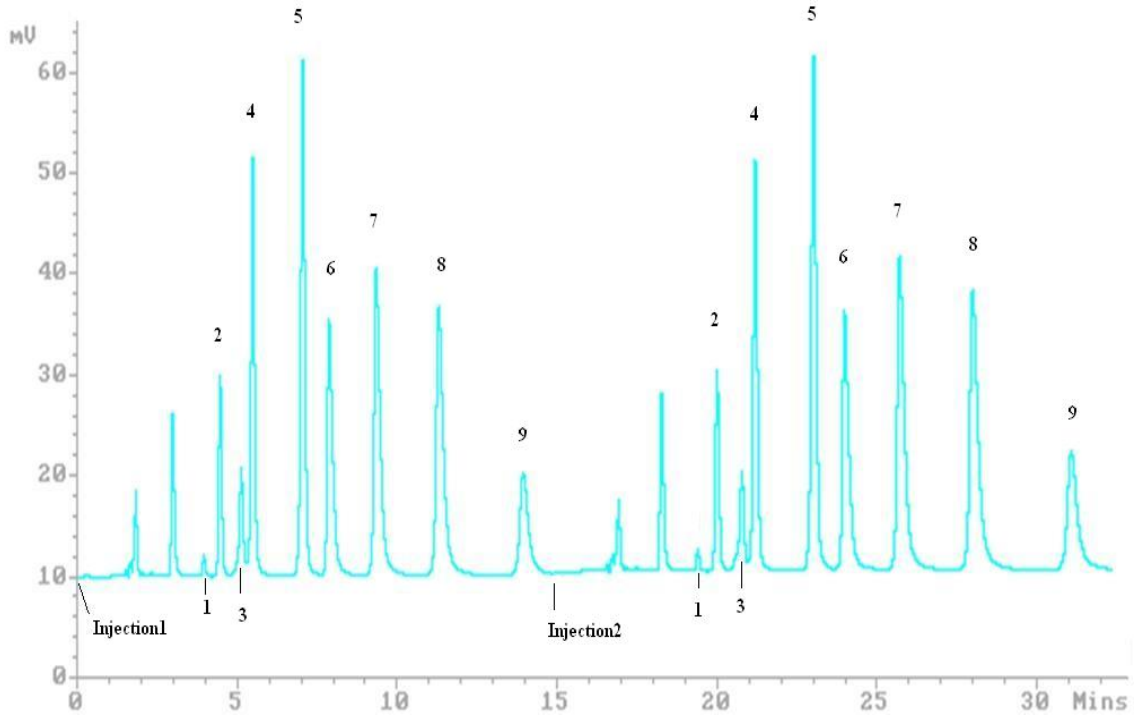

Figure 6. Chromatogram of continuous SLME of a water sample (PH 1.9) containing 80 ng/ml (ppb) nine HAAs: 1: MCAA, 2: DCAA, 3: MBAA, 4: BCAA, 5: DBAA, 6: TCAA, 7: BDCAA, 8: CDBAA, and 9: TBAA. The water sample flow rate was 4 ml/min. The acceptor was 0.05 M tris buffer (PH 8.7) at a flow rate of 0.005 ml/min. Injections were made every 15 min.

Relative standard deviations, enrichment factors, extraction efficiencies and method detection limits (MDLs) were obtained and listed in Table 2. The donor used was a water sample (PH=1.9) containing 21 ppb MCAA, 3 ppb MBAA and 1 ppb other seven HAAs. The donor flow rate was 4 ml/min. The acceptor was 0.05 M tris buffer (PH 8.7) at a flow rate of 0.005 ml/min. The RSDs are between 3.3 and 10.3 %. With this new developed method enrichment factor as high as 500 and MDLs at sub-ppb levels were obtained. With minor modification, this method should also be able to analyze basic compounds in water.

Table 2. **Analytical Performance of continuous SLME-HPLC**

HAAs	RSD* (%)	EF	EE** (%)	MDL*** (ng/ml)
MCAA	10.3	71.3	8.9	6.84
DCAA	10.3	335.5	41.9	0.32
MBAA	3.5	335.9	42.0	0.33
BCAA	4.2	273.6	34.2	0.13
DBAA	4.8	412.1	51.5	0.15
TCAA	5.7	383.4	48.0	0.18
BDCAA	5.9	412.3	51.5	0.18
CDBAA	3.3	428.4	53.6	0.10
TBAA	8.8	305.5	38.2	0.28

*Relative Standard Deviations (RSD) based on seven replications were obtained at concentrations of 21 ppb MCAA, 3 ppb MBAA, and 1 ppb rest 7 HAAs.
**EF and EE were obtained using spiked water samples at the above concentrations.
***The Method Detection Limits (MDLs) were obtained following a standard EPA procedure [3].

References:

1. Shukairy, H. M.; Milter, R. J.; Scott, S. R. J. *AWWA* (1994), 86, 72
2. Kou, D.; Wang, X.; Mitra, S. submitted to *J. Chromatogr. A.* (2004), in review
3. 40 Code *Fed. Register.* **1994**, Part 136, Appendix B.